Available online at www.sciencedirect.com

ScienceDirect

Procedia Materials Science 10 (2015) 572 – 579

Procedia Materials Science

www.elsevier.com/locate/procedia

2nd International Conference on Nanomaterials and Technologies (CNT 2014)

Fabrication of electrospun nanofibers of titanium dioxide intercalated polyaniline nanocomposites for CO_2 gas sensor

Shrikant H. Nimkar, Shikha P. Agrawal, Subhash B. Kondawar*

Department of Physics, Polymer Nanotech Laboratory, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur – 440033, India

Abstract

In this paper we report the synthesis and characterization of nanofibers of titanium-dioxide (TiO_2) intercalated polyaniline (PANI) nanocomposites at room temperature in air at relative humidity of 60% by electrospinning technique. The as-prepared nanofibers were characterized using UV-VIS, FTIR, SEM and XRD. Optical absorbance revealed the shifting of the characteristic peaks for PANI, which may be due to presence of titanium dioxide in PANI matrix. FTIR spectra show the presence of Ti-O-Ti vibrational peak and characteristic vibrational peaks of PANI indicating the interaction of TiO_2 particles with PANI. SEM micrographs revealed the formation of fibers with the diameter less than 200nm. XRD patterns showed the characteristic peaks not only for PANI but also for rutile phase of TiO_2 particles proving the existence of TiO_2 particles within the composites. The as-prepared nanofibers of TiO_2 intercalated PANI nanocomposites when exposed to CO_2 gas (1000 ppm) at room temperature; it was found that the resistance of the nanocomposites was increased from their respective unexposed values. The nanofibers of TiO_2 intercalated PANI nanocomposites were found to be good materials for CO_2 gas sensor even at room temperature as compared to that of pure TiO_2.

Peer-review under responsibility of the International Conference on Nanomaterials and Technologies (CNT 2014)

Keywords: Electrospinning, Titanium dioxide, Polyaniline, Nanocomposites, Nanofibers.

*Corresponding author Tel.: +91-712-2042086;
E-mail address: sbkondawar@yahoo.co.in

1. Introduction

Carbon dioxide (CO_2) in atmosphere contributes to global warming, therefore, there is a great interest by the researchers to detect and monitor carbon dioxide levels in the atmosphere. Carbon dioxide (CO_2) is a colourless, odourless, non-flammable gas that is a product of cellular respiration and burning of fossil fuels. A variety of carbon dioxide sensors have been proposed for measuring carbon dioxide concentration. Usually, the change in the electrical response upon exposure of different carbon dioxide concentrations is used as the technique for carbon

Peer-review under responsibility of the International Conference on Nanomaterials and Technologies (CNT 2014)
doi:10.1016/j.mspro.2015.06.008

dioxide detection. The electrical responses, such as electronic current or capacitance measurement in a resistive-type and capacitance-type sensor play a key role in sensing CO_2 (Chiang et al, 2013). Therefore, research on sensing materials has been focused to design a high performance and elevated efficiency gas sensing elements with suitable sensing materials which can sense high concentration of carbon dioxide (CO_2) gas in atmosphere. Generally, materials for gas sensor can be classified mainly into two main categories i.e. organic and inorganic materials. Semiconducting metal oxides have been well studied for gases detection and considered attractive for their low cost and simple sensing method. However, the high temperature operation of the semiconducting metal oxide based sensor make the lifetime of the sensor shorter and thus required more electricity for operation. Other problems are their poor performance regarding the sensitivity, stability and selectivity at certain low concentration of the gas (Sen et al, 2010). For organic materials category, conducting polymers such as polyaniline, polypyrrole, polythiophene etc. have been widely investigated as effective materials for chemical sensors. Among the conducting polymers polyaniline (PANI) is frequently used because of its ease of synthesis, environmental stability, intrinsic redox reaction, high electrical conductivity and response to acid/base doping, it was thoroughly studied for its application as an active material for gas sensors. However, the problem with these conducting polymers is their low processing ability, poor mechanical strength and chemical stability (Kondawar et al, 2013). There is a tremendous approach for the enhancement of the mechanical strength and characteristics of sensors by combining the organic materials with inorganic counterparts to form composites. Accordingly, organic-inorganic nanocomposite sensors have been developed by several research groups (Pawar et al, 2011), fabricated PANI/TiO_2 nanocomposite ammonia vapor sensor (Deshpande et al, 2009), discovered good sensitivity, reproducibility and faster response to NH_3 at room temperature achieved by using SnO_2/PANI nanocomposites film. Arora et al (2014), studied the effect of fabrication technique on microstructure and electrical conductivity of polyaniline-TiO_2-PVA composite material. Srivastava et al (2011), fabricated TiO_2 doped polyaniline composites for hydrogen gas sensing. Huyen et al (2011), studied effect of TiO_2 on the gas sensing features of TiO_2/PANI nanocomposites. Tai et al (2010), showed comparative studies of Polyaniline (PANI), polyaniline/titanium dioxide (PANI/TiO_2), polyaniline/tin oxide (PANI/SnO_2) and polyaniline/indium oxide (PANI/In_2O_3) thin films developed by using an in-situ self-assembly method for NH_3 gas sensor. Su and Haung (2007), fabricated a humidity sensor based on TiO_2 nanoparticles/polypyrrole composite thin films on alumina substrate and was investigated the humidity sensing mechanism of TiO_2 nanoparticles/PPy composite thin films via the results of activation energy and impedance spectroscopy. Meena et al (2013), fabricated LPG gas sensor using PANI/TiO_2 nanocomposites at 400 ppm. Among the inorganic materials, titanium dioxide (TiO_2) was chosen due to its unique physical and chemical properties such as large energy gap, dielectric constant, and environmental-friendliness and easy to synthesis (Tai et al, 2007). In particular, TiO_2 films have been investigated as sensors for the reducing gas like H_2, LPG, NO_2, CO and NH_3 gases, which react with the negatively charged oxygen adsorbed on the surface of TiO_2 nanoparticles and supplies electrons to the conduction band, leading to a decrease in electric resistance (Deivanayaki et al, 2013).

In the last few decades, there has been significant progress in one-dimensional (1D) nanostructures. Compared to the other dimensions, the first characteristic of 1D nanostructure is its smaller dimension structure and high aspect ratio, which could efficiently transport electrical carriers along one controllable direction, thus are highly suitable for moving charges in integrated nanoscale systems. The second characteristic of 1D nanostructure is its device function, which can be exploited as device elements in many kinds of nanodevices (Lu et al, 2011 and Long et al, 2011). It has been found that the nanofibers significantly improve the processability of polyaniline and its performance in many conventional applications involving polymer interactions with its environment. This leads to much faster and more responsive chemical sensors and new inorganic/polyaniline nanocomposites (Haung et al, 2006). Large numbers of advanced techniques have been developed to fabricate one dimensional (1D) nanostructures with well controlled morphology and chemical composition. Among these methods, electrospinning seems to be the simplest and most versatile technique capable of generating (1D) nanostructures from variety of polymers. Compared to the commercial mechanical spinning process for generating microfibers, electrospinning mainly makes use of the electrostatic repulsions between surface charges to reduce the diameter of a viscoelastic jet or a glassy filament (Soujanya et al, 2014). Other advantages of the electrospinning technique are the liability to control the fiber diameters, the high surface-to-volume ratio, high aspect ratio, and pore size as non-woven fabrics. Moreover, nanofibers of composites can easily be made via the electrospinning technique with the only restriction being that the second phase needs to be soluble or well dispersed in the initial solution (Lu et al, 2009). This led to the idea of fabricating Polyaniline/Titanium Dioxide nanofibers which can work at room temperature as

chemiresistive sensors. To the best of our literature survey in the field of nanofibers of composites based CO_2 gas sensors, there is no work reported on nanofibers of composites of conducting polymer and titanium dioxide based CO_2 gas sensors. Therefore, we report in this paper the fabrication of electrospun nanofibers of Polyaniline (PANI)/TiO_2 nanocomposites by electrospinning technique and their sensing behaviour for CO_2 gas. The synthesized nanofibers were also subjected to various characterizations such as UV-VIS Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) to understand the interaction between PANI and TiO_2 and the morphology of composite.

2. Experimental

2.1Materials

Aniline monomer was distilled under reduced pressure prior to use. Aniline (99.5%), Titanium trichloride ($TiCl_3 \cdot 9H_2O$) (99%), hydrogen peroxide (H_2O_2) (99.5%) were procured from E. Merck. Ammonium per sulphate (APS) (98%) and N-N Dimethylformamide (DMF) (99.5%) were purchased from Hi-media and used as received. All chemicals were of analytical grade and solutions were prepared with double distilled water (DDW).

2.2 Synthesis of titanium dioxide/polyaniline nanocomposites

Solution - route technique was employed to synthesize titanium dioxide (TiO_2)/polyaniline (PANI) nanocomposites, (Deshpande et al, 2009). In this technique, formation of nanocomposites proceeds through an inorganic/organic interface reaction.. Initially, 0.4M $TiCl_3 \cdot 9H_2O$ was dissolved in 50ml double distilled water (DDW) with constant stirring and pH of the solution was maintained at ≤ 4 using 1M HCl. Hydrogen peroxide (2ml) was added in the above solution, which oxidized titanium ions to titanium dioxide, and the solution turns reddish suspension of TiO_2. It was used as the starting reaction mixture for further processing. The above solution was then mixed with 0.2M aniline and kept below 4^oC. After 30min, 0.2M APS solution was added in the above mixture to make the reaction bath mixture. It was found that after few minutes the solution colour turned bluish to green, which mark the formation of polyaniline nanocomposite. The precipitate was washed thoroughly using DDW and dried at 70^0C in vacuum oven. The obtained powder was conductive emeraldine salt (ES) form of PANI/TiO_2. For emeraldine base (EB), PANI/TiO_2 (ES) was kept in 0.1 M ammonia solution and stirred overnight at room temperature. The precipitate was filtered and washed with DDW until filtered solution became neutral and then dried in vacuum for 24 h to obtain emeraldine base (EB) form of PANI/TiO_2 nanocomposite.

2.3 Fabrication of Electrospun nanofibers of titanium dioxide/polyaniline nanocomposites

1% PANI/TiO_2 nanocomposite was mixed with 10% Polyvinyl Alcohol (PVA) as carrier polymer so as to make the desired viscous solution for loading into syringe to fabricate electrospun nanofibers. In a typical procedure, the PANI/TiO_2 (EB) nanocomposite powder was separately mixed with Camphor Sulfonic Acid (CSA) by grinding in a smooth agate mortar so as to make the composite soluble with good electrical conductivity. The CSA doped PANI/TiO_2 nanocomposite was separately dissolved in DMF. Later, the solution was magnetically stirred for 12 hours to get uniformly mixed solution. Then, doped PANI/TiO_2 nanocomposite was electrospun by laboratory set up electrospinning apparatus (figure 1). It consists of a syringe pump, DC high voltage source and rotating cylindrical collector. The spinning solution was kept in a vertical syringe with a stainless steel needle having an orifice of 0.55 mm. The needle was electrically connected to a positive high voltage. The rotating cylindrical collector of diameter 30 mm was placed below the syringe connected to ground. Electrospinning was carried out at room temperature in air at relative humidity of 60% in an insulated box. The positive high voltage of 20 kV was applied to the needle. The rotational speed of the rotating cylindrical collector during electrospinning was kept at 1000 rpm and the solution flow rate was maintained at 0.2 ml/h using computer control programmer (Dhakate et al, 2011, 2010). The fibers were collected on aluminium foil of thickness 0.5mm wrapped on cylindrically rotating collector.

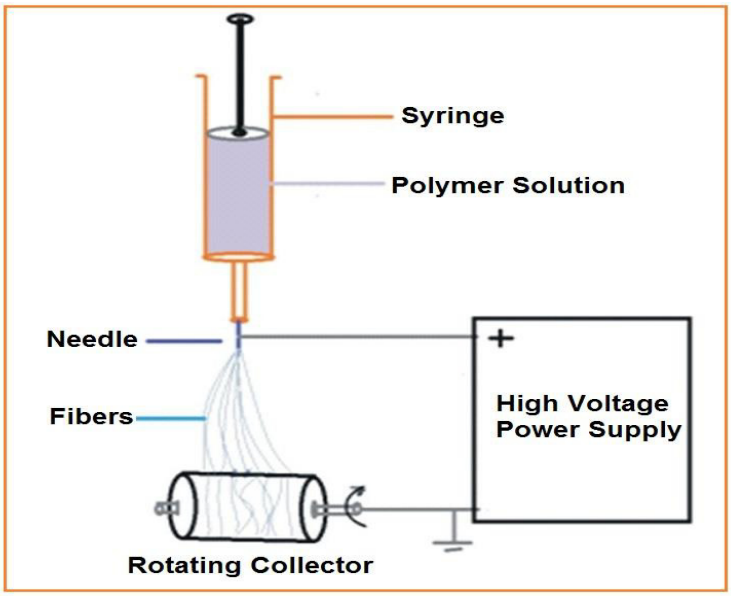

Fig. 1. Schematic diagram of electrospinning used for nanofibers fabrication

3. Results and discussion

3.1. UV-Vis Spectroscopy

Absorbance spectra of PANI/TiO_2 nanofibers were recorded in the range of 200 – 800 nm by using UV-1800 double beam UV-Vis Spectrophotometer. Generally, conducting polymers have a broad UV-Vis absorption band, due to the wide distribution of conjugated chain length of conducting polymers. The UV-Vis spectrum of the PANI/TiO_2 nanocomposite nanofibers is shown in Fig. 2(a). The three characteristic bands appear at about 290, 355 and 560nm. The peak at 290nm which is attributed to π-π* transitions and is also the characteristic peak of pure Polyaniline (PANI) as reported (Lu et al, 2006 and Shahi et al, 2011). The peak at 355nm appears due to the UV absorbance by TiO_2 nanoparticles. The peak appears at the 560nm which is attributed to polaron- π* transition. It is polaronic band transition which is due to the inter-ring charge transfer associated with excitation from benzenoid to quinoid units (Nubert et al, 2011 and Tomer et al, 2005). Optical absorbance studies show the shifting of the characteristic peaks for PANI, which may be due to presence of titanium dioxide in PANI matrix.

3.2. Fourier Transform Infrared (FTIR) Spectroscopy:

Infrared spectra of PANI/TiO_2 nanofibers were recorded using Bruker - α Fourier Transform Infrared Spectrometer. The FTIR spectra of PANI and PANI/TiO2 nanocomposite nanofibers are shown in Fig. 2(b). The broad peak at 3434cm^{-1} is attributed to N-H stretching mode. The vibration band seen around 2930-2932cm^{-1} has been ascribing to the aromatic C-H vibration. The 1590-1650cm^{-1}vibration band is due to the C-N stretching vibration of quinoid rings whereas 1439-1498cm^{-1} vibration band arises due to the C-N stretching vibration associated with the benzenoid ring. In the region close to 1350cm^{-1} the peaks are attributed to the presence of aromatic amines present in polyaniline. The band at 1251-1254cm^{-1} linked with various stretching and bending vibrations associated with C-N single bond. The vibration band at 1100-1050cm^{-1} range is the characteristic band of PANI corresponding to charge delocalization proving the protonation which is shifted towards higher wavelength side due to the interaction of TiO_2 in PANI matrix. It is also observed that the peaks at around 800-850cm^{-1} corresponds to the C-H bending out of the plane for 1, 4 substituted aromatic ring indicating the linear structure which is slightly deviated due to the

presence of TiO_2 particles. There is a weak band around 650-670cm^{-1} which is due to the Ti-O stretching (Qui and Yu 2008).

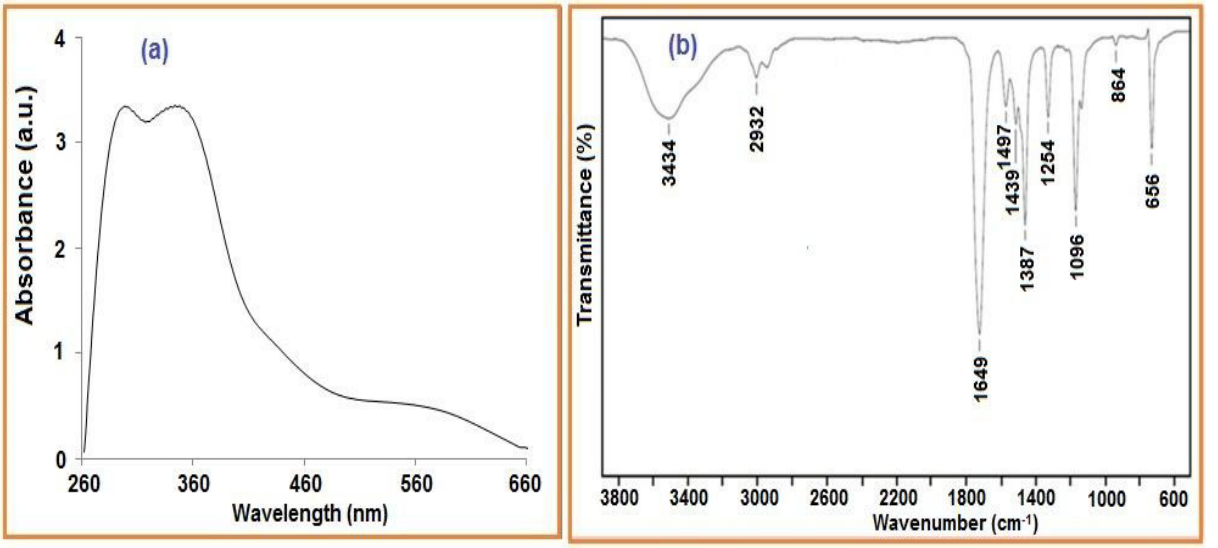

Fig. 2. (a) UV-VIS spectrum and (b) FTIR spectrum of PANI/TiO_2 nanofibers

3.3. X-ray Diffraction (XRD):

The X-Ray Diffraction patterns were recorded on Automatic X-Ray Diffractometer using Cu-Kα radiation of wavelength 1.54Å. The XRD pattern of TiO_2 intercalated PANI is shown in Fig. 3(a). Pattern show the characteristic peaks not only for the PANI but also for the TiO_2 nanoparticles, proving the existence of TiO_2 nanoparticles within the nanocomposite. The broad amorphous peak is seen, but its intensity decreased, which implied that the nanocomposite has a more ordered arrangement than the bare polymer owing to the TiO_2.

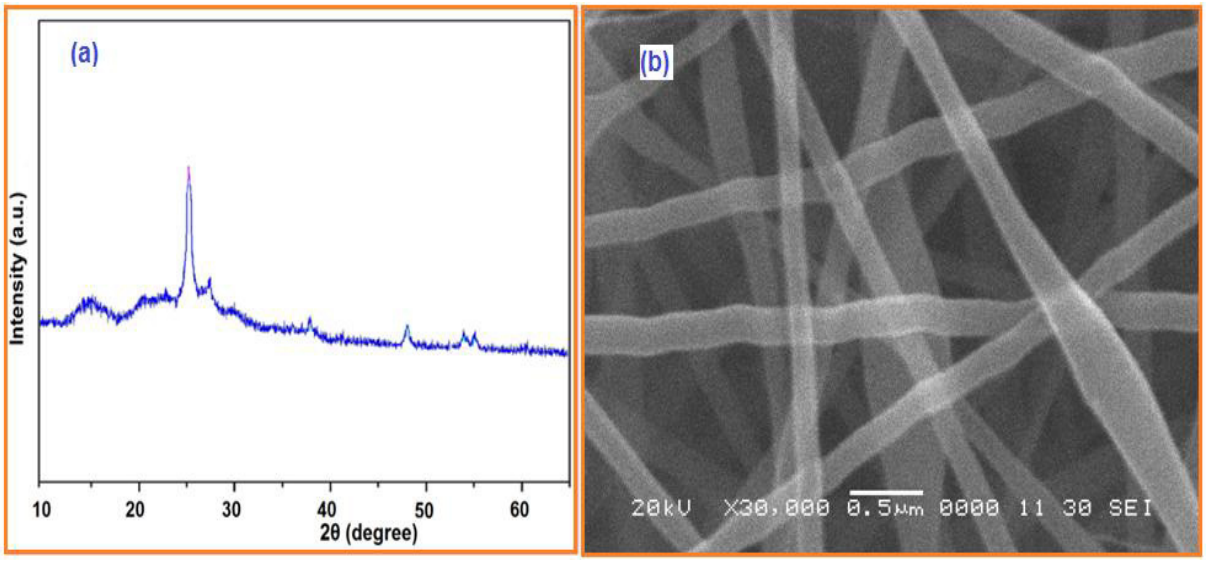

Fig. 3. (a) XRD pattern and (b) SEM image of PANI/TiO_2 nanofibers

On comparing the observed XRD peaks and corresponding planes with the standard (h k l) planes, good matching was seen between the two sets, confirming that the nanofibers consist of TiO_2 having rutile phase (ICDD DATA CARD 21-1276). The XRD pattern for titanium dioxide and polyaniline nanofibers showed diffraction peaks along (1 1 0), (1 0 1), (1 1 1), (2 1 1), (2 2 0) respectively. The peaks related to the TiO_2 nanoparticles centered at 2θ = 23.68°, 26.28°, 37.62°, 48.02° and 54.32° became more sharp and crystalline. These peaks are slightly shifted, from their respective standard positions, may be due to presence of PANI matrix as reported earlier (Zhang et al, 2010, Zhampetti et al, 2012 and Lee et al, 2012).

3.4. Scanning Electron Microscopy (SEM)

The surface morphology was studied by using JEOL-JSM-6390LV Scanning Electron Microscope. The morphology of PANI/TiO_2 nanofibers was investigated by SEM. From the SEM micrograph as shown in Fig. 3(b), it is seen that the smooth nanofibers with several millimeters length and an average diameter, in the range of about 200nm to 300nm are formed. The irregularities in the nanofibers could be due to the incompatibility of the two components present in the nanocomposites (Ansari and Mahamad, 2011, Haldorai et al, 2008).

3.5. CO_2 gas sensing

The gas sensing behavior of chemiresistor sensors was studied by calculating change in the surface resistance of sensing film with temperature in the range of 30 – 60 °C toward pure air and CO_2 gas exposure. The resistance variation was measured by Keithley 2000 multimeter and temperature was controlled by 'Temperature Controlled VI Characterization System'. The chemiresistor type sensor was mounted on hot plate (filament heater) which was coupled with ceramic base stand. The two electrodes were attached to PANI/TiO_2 nanofibers film which was deposited on glass substrate. Finally this sensor setup was fixed into the homemade glass chamber. The electrical connections for gas sensing measurements, thermocouple and temperature variation were made using instrumentation feed through. The gas sensing setup used to measure variation in resistance as shown in Fig. 4. PANI/TiO_2 nanofibers film was exposed to 1000 ppm CO_2 gas and the sensitivity of the film was determined in temperature range 30-60 °C to know the highest response at lower operating temperature.

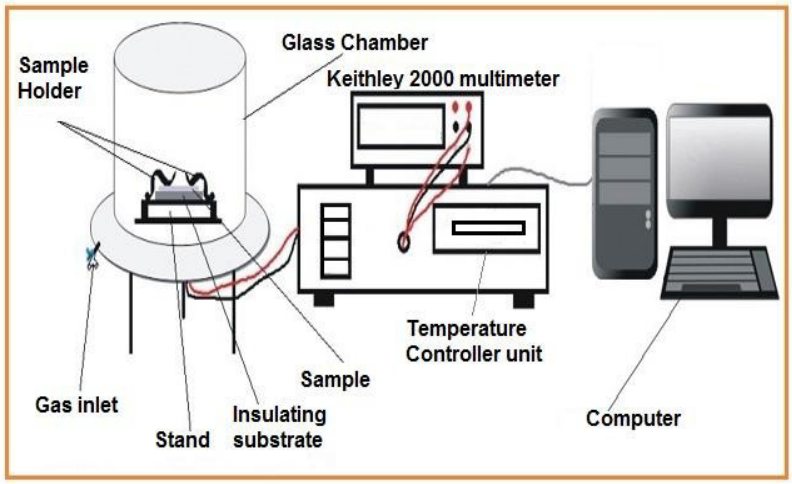

Fig. 4. Laboratory set up for gas sensing

Fig. 5(a) shows the variation of sensitivity of the sensor for CO_2 gas with the temperature. On exposing the PANI/TiO_2 nanofibers film with CO_2 gas which can be permeated into the PANI matrix freely and some of the CO_2 molecules might reach into the depletion region, which is surrounding the TiO_2 crystallite. PANI and TiO_2 may form a p–n junction and the observed increased sensitivity of the film may be due to the creation of a positively charged depletion layer on the surface of TiO_2 which could be formed owing to inter-particle electron migration from TiO_2 to

PANI at the heterojunction. This would cause a reduction of the activation energy and enthalpy of physisorption for CO_2 gas (Tai et al, 2007). The surface morphology of PANI/TiO_2 film is nanofibrous, which seem to contribute to the short response time and good reversibility of the sensors. This is due to the fact that gas diffusion occurs more easily in nanofibrous structures, which significantly enhanced the diffusion due to its larger exposure area and penetration depth for gas molecules (Li et al, 2004). Therefore, the response and sensitivity of the PANI/TiO_2 nanofibers film sensor increased due to its high aspect ratio apart from its high surface-to-volume ratio.

The response/recovery time is an important parameter for characterizing a sensor. Response of PANI/TiO_2 nanofibers for CO_2 gas at 1000 ppm with respect to time is shown in Fig. 5(b). The response time of PANI/TiO_2 nanofibers film for 1000 ppm CO_2 gas at 48 ^oC (highest sensitivity operating temperature) was found to be ~80 second. After the ~5 min of CO_2 exposure, a CO_2 desorption experiment was conducted by exposing the PANI/TiO_2 nanofibers film to an air environment without CO_2. An exponential decrease in the sensitivity with a short recovering time of nearly ~100 second was observed. The time constant for CO_2 desorption was significantly larger than that for the adsorption, indicating the difference in the adsorption and desorption kinetics.

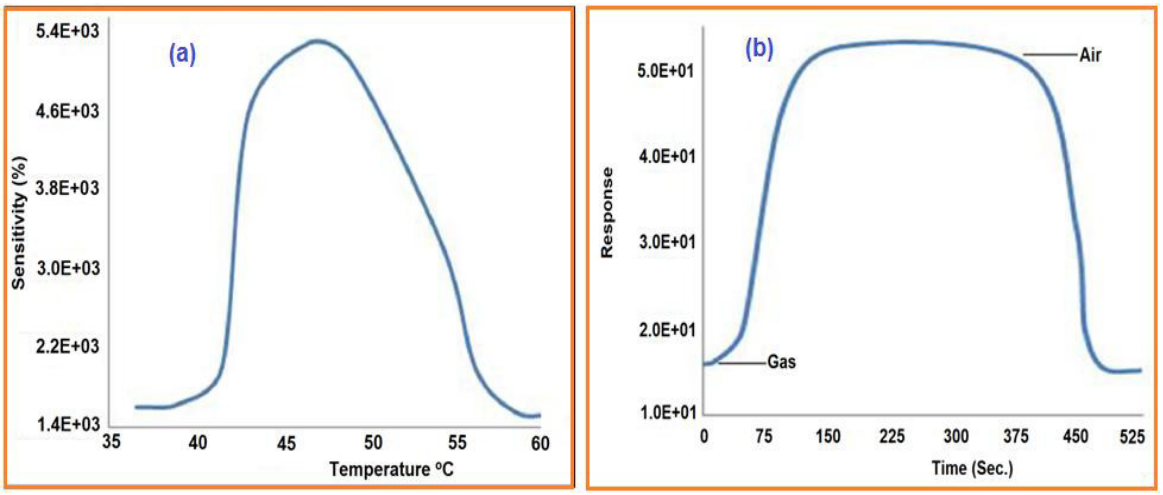

Fig. 5. (a) Sensitivity and (b) Response of PANI/TiO_2 nanofibers for CO_2 gas at 1000ppm

4. Conclusion

The electrospun nanofibers of PANI/TiO_2 nanocomposite are prepared successfully via electrospinning technique. FTIR, UV-VIS and XRD revealed the good interaction between PANI and TiO_2 nanoparticles and confirmed the formation of nanocomposite. SEM image showed the nanofibers of PANI/TiO_2 nanocomposite with the average diameter 250 nm. The nanofibers of PANI/TiO_2 nanocomposite exhibited high sensitivity for CO_2 gas at 1000 ppm at low operating temperature around 48^oC.

Acknowledgements

The authors acknowledge University Grants Commission, New Delhi (India) for financial assistance under Major Research Project, UGC File No: 39-540/2010(SR).

References

Ansari, M., and Mohammad, F., 2011, Thermal stability, electrical conductivity and ammonia sensing studies on p-toluenesufonic acid doped polyaniline: titanium dioxide (pTSA/Pani: TiO_2) nanocomposites, Sensors and Actuators B, 157, 122-129.

Arora, R., Mandal, U., Sharma, P., Srivastav, A. 2014, Effect of fabrication technique on microstructure and electrical conductivity of polyaniline-TiO_2-PVA composite material, Procedia Materials Science, 6, 238–243.

Chiang, C. J., Tsai, K. T., Lee, Y. H., Lin, H. W., Yang, Y. L., Shih, C. C., 2013, In situ fabrication of conducting polymer composite film as a chemical resistive CO_2 gas sensor, Microelectronic Engineering, 111, 409-413.

Deivanayaki, S. Ponnuswamy, V., Ashokan, S., Jayamurugan, P., Mariappan, R., 2013, Synthesis and characterization of TiO_2-doped Polyaniline nanocomposites by chemical oxidation method, Materials Science in Semiconductor Processing, 16, 554-560

Dhakate, S.R., Gupta, A., Chaudhari, A., Tawale, J., Mathur, R., 2011, Morphology and thermal properties of PAN copolymer based electrospun nanofibers, Synthetic Metals, 161, 411-419.

Dhakate, S.R., Singla, B., Uppal, M., Mathur, R.B., 2010, Effect of processing parameters on morphology and thermal properties of electrospun polycarbonate nanofibers, Advanced Materials Letters, 1(3), 200-204.

Haldorai Y, Park, E.J., Gal, Y.S., Lim, K.T., 2008, Synthesis and characterization of polypyrrole-TiO_2 nanocomposites in supercritical CO_2, Colloids and Surfaces A: Physiochemical Engineering Aspects, 313, 300-303

Huang, J., 2006, Syntheses and applications of conducting polymer polyaniline nanofibers, Pure Applied Chemistry, 78(1), 15-27

Huyen, D.N., Tung, N.T., Thien, N.D., Thanh, L.H., 2011, Effect of TiO_2 on the Gas Sensing Features of TiO_2/PANi Nanocomposites, Sensors, 11, 1924-1930.

Kondawar S. B., S. Agrawal, S. P., Nimkar, S. H., Sharma, H. J., Patil, P. T., 2012, Conductive polyaniline tin-oxide nanocomposites for ammonia sensor, Advanced Materials letters, 3(5), 393-398.

Lee, S.S., Bai, H., Liu, Z., Sun, D.D., 2012, Electrospun TiO_2/SnO_2 nanofibers with innovative structure and chemical properties for highly efficient photocatalytic H_2 generation, International journal of hydrogen energy, 37, 10575-10584.

Long, Y.Z., Li, M.M., Gu, C., Wan, M., Duvail, J.L., Liu, Z., Fan, Z., 2011, Recent Advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers, Progress in Polymer Science, 36, 1415-1442.

Lu, X., Zhao, Q., Wang, D., Wang, C., 2006, Preparation and characterization of Polypyrrole/TiO_2 Coaxial Nanocables, Macromolecule Rapid Communication, 27, 430-434

Lu, X., Zhang, W., Wang, C., Wen, T.C., Wei, Y., 2011, One-dimensional conducting polymer nanocomposites: Synthesis, properties and applications, Progress in Polymer Science, 36, 671–712.

Lu, X., Wang, C., Wei, Y., 2009, One-Dimensional Composite Nanomaterials: Synthesis by Electrospinning and Their Applications, Small, 5 (21), 2349-2370.

Li, X., Wang, G., Lu, D., 2004, Surface properties of polyaniline/nano TiO_2 composites, Applied Surface Science, 229, 395-401

Meena, P.A., Koppalkar, A., Roy, A. S., 2013, Liquefied Petroleum Gas Sensing of Polyaniline-Titanium Dioxide Nanocomposites, Sensor Letters, 11, 242-250.

Neubert, S., Pliszka, D., Thavasi, V., Wintermantel, E., Ramakrishna, S., 2011, Conductive electrospun PANi-PEO/TiO_2 fibrous membrane for photo catalysis, Materials Science and Engineering B, 176, 640–646

Pawar S. G., Chougule, M. A., Patil, S. L., Raut, B. T., Ghodse, P.R., Sen, S., Patil, V. B., 2011, Room temperature ammonia gas sensor based on polyaniline – TiO_2 nanocomposites, Sensors & Transducers, 125(2), 107-112.

Qiu, Y. and Yu, J., 2008, Synthesis of titanium dioxide nanotubes from electrospun fiber templates, Solid State Communications, 148, 556-558

Soujanya, G.K., Hanas, T., Chakrapani, V.Y., Ratna Sunil, B., Sampath Kumar, T.S., 2014, Electrospun Nanofibrous Polymer Coated Magnesium Alloy for Biodegradable Implant Applications, Procedia Materials Science, 5, 817–823.

Sen, S., Kanitkar, P., Sharma, A., Muthe, K.P., Rath, A., Deshpande, S.K., Kaur, M., Aiyer, R.C., Gupta, S.K., Yakhmi, J.V., 2010, Growth of SnO_2/W18O49 nanowire hierarchical heterostructure and their application as chemical sensor, Sensors and Actuators B, 147, 453–460**.**

Shahi, M., Moghimi, A., Naderizadeh, B., Maddah, B., 2011, Electrospun PVA–PANI and PVA–PANI–$AgNO_3$ composite nanofibers, Scientia Iranica C, 18, (6), 1327–1331

Srivastava, S., Singh, V.N., Singh, M., Vijay, Y.K., 2011, Synthesis and characterization of TiO_2 doped polyaniline composites for hydrogen gas sensing, International Journal of Hydrogen Energy, 36, 6343-6349

Su, P.G., Huang, L.N., 2007, Humidity sensors based on TiO2nanoparticles/polypyrrole composite thin films, Sensors and Actuators B, 123, 501-509

Tai, H., Jiangy, Y., Xie, G., Yu, J., 2010, Preparation, Characterization and Comparative NH_3-sensing Characteristic Studies of PANI/inorganic Oxides Nanocomposite Thin Films, Journal of Matererial Science and Technology, 26(7), 605-611.

Tai, H., Jiang, Y., Xie, G., Yu, J., Chen, X., 2007, Fabrication and gas sensitivity of polyaniline–titanium dioxide nanocomposite thin film, Sensors and Actuators B, 125, 644-650.

Tomer, V., Tokash, J.C., Reneker, D.H., Ramsier, R.d., 2005, Selective emitters for thermophotovoltaics: erbia –modified electrospun titania nanofibers, Solar Energy Materials & Solar Cells, 85, 477-488.

Zampetti, E., Bearzotti, A., Macagnano, A., 2012, UV assisted chemical sensor based on Electrospun Titania nanofibers working at room temperature, Procedia Engineering, 47, 912 – 915.

Zhang, Z., Shao, C., Zhang, L., Li, X., Liu, Z., 2010, Electrospun nanofibers of V-doped TiO_2 with high photocatalytic activity, Journal of Colloid and Interface Science, 351, 57–62.